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Low temperature thermochemical treatment of stainless steel; bridging from science to technology

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Abstract

The present contribution gives an overview of some of the fundamental scientific aspects of low temperature thermochemical treatment of stainless steel, in particular the characterisation of so-called expanded austenite is addressed. Selected technological examples of thermochemical treatment of stainless steel are presented.

1. Introduction

Stainless steel is a widely applied material in applications where corrosion resistance is of importance. The corrosion resistant nature of stainless steels has its origin in the presence of the alloying element Cr, which forms a very stable passive layer that protects the steel. Unfortunately, stainless steel suffers from extensive wear e.g. galling, which hinders a wider applicability of the material and may cause problems in existing applications.

In the early- and mid-eighties it was discovered that it was possible to dissolve large quantities of nitrogen or carbon in stainless steel at low temperature. This discovery coincided with the upcoming of plasma-based nitriding/carburising techniques, and thus – to some extent - became associated with this technology. The resulting surface structures of low-temperature treated stainless steel proved exceptionally wear resistant and the corrosion resistance was unaltered or even improved. The microstructural feature responsible for the highly demanded combination of excellent corrosion and wear performances has generally been named S-phase or expanded austenite, γ_N . In this text the name/term “expanded austenite” is abandoned and replaced by *expanite*.

Expanite is obtained when high amounts of atomic nitrogen and/or carbon are dissolved in stainless steel at temperatures below approximately 450-550°C depending on the type of interstitial. The interstitial atoms are presumed to reside in the octahedral interstices of the f.c.c. lattice [1]. Typically, nitrogen contents in nitrided stainless steel range from 20 to 30 at.% N; carbon contents in carburised stainless steels are typically below 15 at.% C. Such high contents of interstitials are obtained, because of the relatively strong affinity of Cr atoms for N/C, leading to short range ordering of Cr and N/C. Due to the low mobility of Cr atoms as compared to the interstitial atoms at low treatment temperatures, chromium nitrides/carbides do not precipitate until after long exposure times and the interstitials are kept in solid solution by the Cr “trap sites”.

Within the last 10 years various methods for in-situ and ex-situ treatments for *gaseous* thermochemical processing of stainless steels have been developed by the present authors. These methods allow thermodynamically controlled formation of expanite “layers” contrary to hitherto applied plasma based methods. The present contribution offers an overview on the various scientific

results obtained by the developed methods for gaseous thermochemical processing and some technological examples of surface hardening of stainless steel are presented.

2. Gaseous surface hardening of stainless steel

In micrographs expanite is typically recognized as a featureless surface “layer” (Fig. 1) with hardness values reaching almost 1400 HV [2]. The featureless nature of γ_N compared to the clearly distinctive nature of the austenite substrate is a result of selective etching; γ_N has a higher electrochemical potential than the nitrogen-free austenitic substrate.

Obviously, the gas composition determining the so-called nitriding potential, $K_N = p_{NH_3} / p_{H_2}^{3/2}$, which is proportional to the nitrogen activity, a_N , plays a major role with respect to formation of γ_N “layers” (cf. Fig. 1). The gas composition controls the surface nitrogen concentration in the stainless steel (assuming local equilibrium between gas and solid phase) and hence the growth kinetics of the γ_N case.

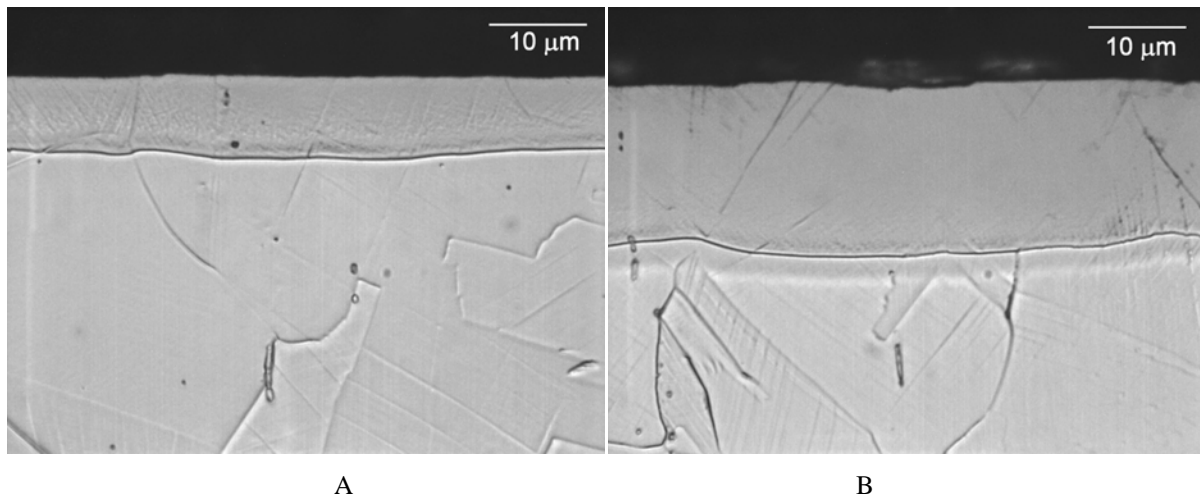


Figure 1. Micrographs of AISI 316 nitrided at 445°C for 22 hours A) $K_N = 0.293 \text{ bar}^{-1/2}$ and B) $K_N = 2.49 \text{ bar}^{-1/2}$

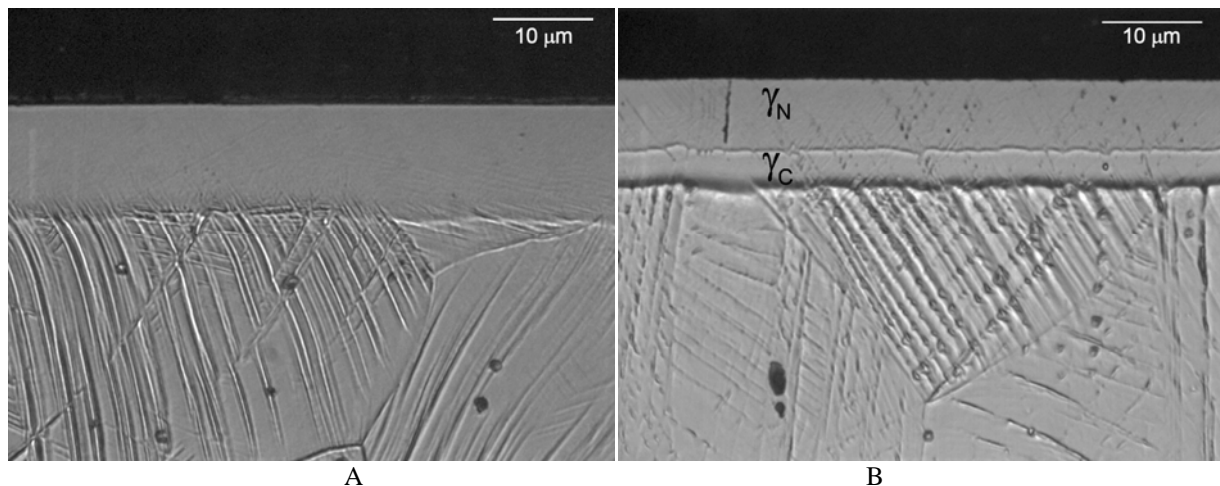


Figure 2. Micrographs of A) Cold worked AISI 316 carburised at 420°C for 17 hours and 15 minutes in 5.3% C_2H_2 -8.6% N_2 -86.1% H_2 and B) AISI 304 nitrocarburised in 14% C_3H_6 - 54% NH_3 - 22% H_2 -10% Ar at 420 °C for 19 hours.

Micrographs of carburised and nitrocarburised (cold worked) stainless steels are given in Fig. 2. The transition from the substrate to the γ_C zone for the carburised samples in Fig. 2A is smooth and not as pronounced as is observed for nitriding, which can be attributed to a continuous carbon

solubility in γ_C contrary to the “discontinuous” behaviour observed for nitrogen (see below). The grain boundaries from the austenite substrate continue into γ_C – fading out as the surface is approached (higher C contents). The chemical resistance of γ_C to the etching reagent is clearly observed; the γ_C zone appears featureless contrary to the substrate. This phenomenon, as for nitriding, hints at a higher electrochemical potential of γ_C as compared to austenite in the etchant applied.

The combination treatment (Fig. 2B) produces a “duplex layer” of expanite of approximately 12 μm . The layer consists actually of two separate zones with a somewhat diffuse transition; the outer zone is γ_N and the inner zone is γ_C . The γ_N zone is significantly larger than the γ_C zone. This can directly be attributed to the applied gas composition, i.e. the imposed nitrogen and carbon activities. The application of unsaturated carbon gas, i.e. propene, and NH_3 allows direct control of the thermodynamics. Consequently, tailoring of a combination of γ_N and γ_C may indeed be possible, which also implies larger flexibility in tailoring the materials properties.

3. Solubility of N/C in expanite.

The relation between nitrogen content and gas composition was established from equilibrating thin foils of stainless steel AISI 304 and 316 in accurately controlled NH_3/H_2 gas mixtures in a thermobalance, determining the equilibrium nitrogen contents from weight changes [3]. The results are given in Fig.3A, which shows a unique relation between nitrogen occupancy of the octahedral interstices, y_N , and the adjusted nitrogen activity in the gas phase, a_N . It was also observed that nitrogen contents lower than $y_N=0.17$ could not be retracted from the samples, not even in pure H_2 , which is a consequence of relatively strong bonding to Cr (which occupy 17 % of the f.c.c. host lattice), i.e. short range order [4].

The data in Fig. 3A demonstrates convincingly that, colossal quantities of nitrogen can be dissolved reproducibly by imposing a nitrogen activity adjusted through the nitriding potential, K_N , of the gas mixture and the temperature of the sample.

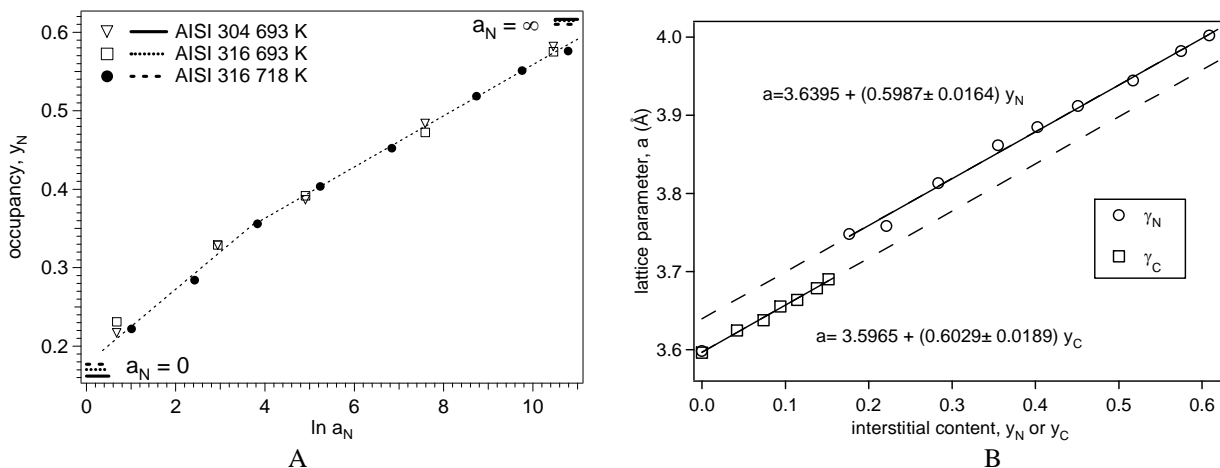


Figure 3. A) Solubility of nitrogen (interstitial occupancy, y_N) in expanite as a function of nitrogen activity. B) The lattice parameter of homogeneous expanite as a function of nitrogen and carbon content.

Absorption isotherms as shown for γ_N in Fig. 3A have so far not been published for γ_C . Recent work indicates that the maximum solubility in carbon expanded austenite in para-equilibrium cannot exceed approximately $y_C=0.16$; beyond this carbon content carbides develop [5]. The underlying chemical or physical reasons for these observations remain to be unravelled.

The lattice expansion (Fig. 3B) associated with the colossal dissolution of nitrogen and carbon implies the occurrence of large stresses and steep stress gradients over a growing layer of expanded

austenite. Compressive stresses of nearly 8 GPa's and stress gradients of the order of a 10^{15} Pa.m⁻¹ are no exception [6,7].

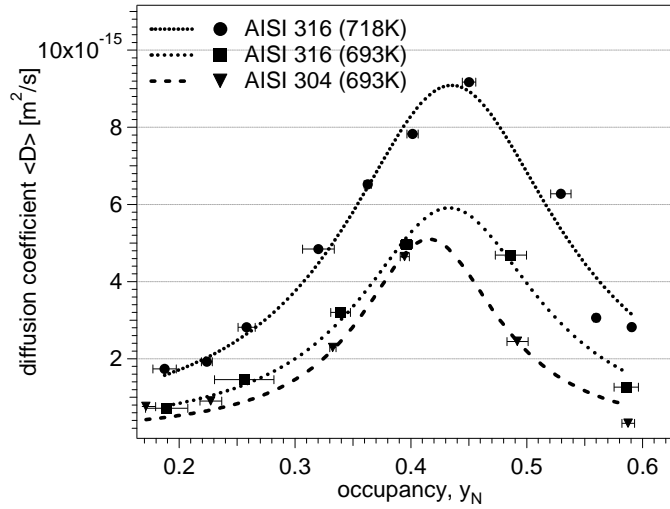


Figure 4. Experimentally determined nitrogen diffusion coefficient in expanite as a function of composition.

4. Nitrogen diffusion in expanite

As mentioned above thin foils were nitrided in a thermobalance for continuous monitoring of the change of the sample weight and thus the nitrogen content. After equilibrating in pure NH₃ the samples were equilibrated at a slightly lower a_N , by adjusting the composition of the NH₃/H₂ gas mixture. Consequently, the sample weight decreases by denitriding. Applying the equation for desorption from a plate, taking the presumed constant diffusivity as a fitting parameter an effective value for the diffusion coefficient in the composition range is obtained. The influence of stress (gradients) on this value is small. By controlled denitriding in a stepwise fashion the composition range of expanite can be investigated and the diffusion coefficients obtained in each step reflect the diffusivity as a function of nitrogen content [7].

The effective diffusivities thus obtained are depicted in Fig. 4. Evidently, the diffusion coefficient of nitrogen in expanite is concentration dependent and has a maximum value for nitrogen occupancies of about $y_N=0.45$. Qualitatively, these results can be reasoned as follows. The expansion of the austenite lattice by dissolution of nitrogen is likely to facilitate the transfer of a nitrogen atom from an octahedral interstitial site of the f.c.c. lattice to a tetrahedral site, which can be considered the activated state for interstitial diffusion in f.c.c. lattices. Thus the activation energy for diffusion of nitrogen is reduced. With increasing nitrogen content the occupancy of the interstitial lattice increases, which reduces the probability that a nitrogen atom in the activated state can jump to an unoccupied octahedral site. Consequently, the diffusion coefficient decreases.

5. Thermal stability of expanite

Decomposition of expanite, which is a thermally activated process, involves precipitation of chromium nitrides or chromium carbides. As a consequence, chromium is retracted from solid solution and the favourable corrosion properties of the stainless steel (expanite) are lost. Fig. 5A shows a partly decomposed γ_N layer wherein CrN has precipitated (dark regions) along grain boundaries and along the surface in nitrided AISI 316.

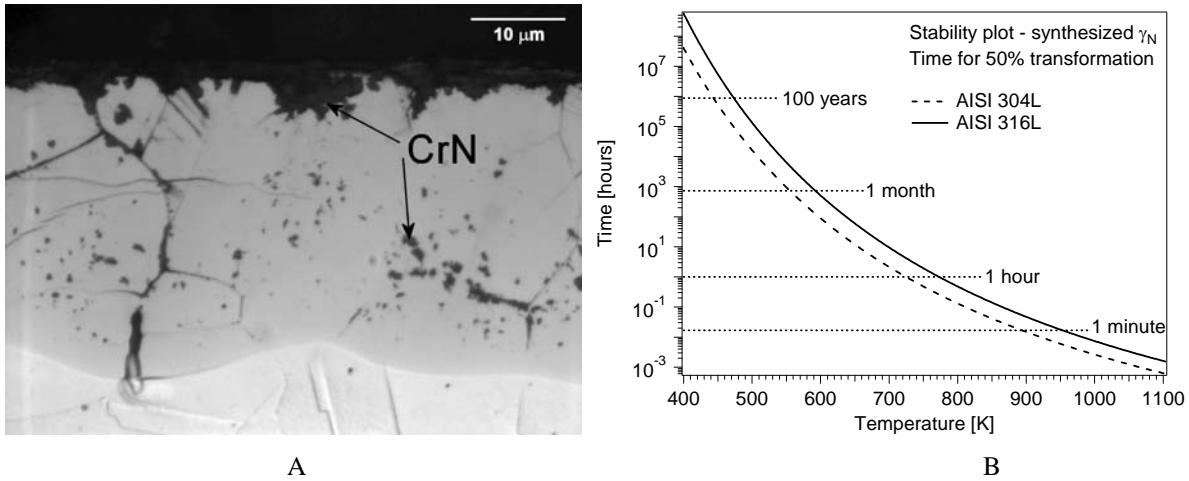


Figure 5. A) Micrograph of AISI 316 nitrided for 21 hours at 480°C ($K_N = \text{inf}$). B) Stability plot (temperature-time) of γ_N in AISI 304L and AISI 316L.

In order to characterise the decomposition kinetics of nitrogen expanded austenite, homogenous stress free synthesised γ_N powder (AISI 304L & 316L) with controlled nitrogen content was subjected to thermal analysis in a thermal analyzer [8]. Based on experimental non-isothermal results, the isothermal stability of nitrogen expanded austenite was calculated (Fig. 5B).

Clearly, the presence of Mo in AISI 316L in comparison to AISI 304L has a significant effect on the thermal stability of γ_N as the decomposition temperature is shifted to higher temperatures. It is also obvious from Fig. 5B that the process parameters temperature and time for nitriding are a compromise between fast development of a γ_N zone and slow development of CrN precipitates during treatment.

In Fig. 6 X-ray diffraction patterns (collected at room temperature) of γ_C isochronally heated to twenty different temperatures are presented. The figure illustrates the development of carbide precipitation as a function of temperature. The temperature resolved analysis allows for a detailed insight into the chronology of the carbide precipitation sequence occurring in thermally exposed expanite. The precipitation of $M_{23}C_6$ happens more or less continuously from 647°C (920K) to 767°C (1040K), this is verified by the reflection around 58 degrees increasing in intensity. Reaching 817°C (1090K) the XRD reflection at 60 degrees pertaining to M_7C_3 is developing. A detailed analysis and discussion of carbide precipitation in carbon expanite can be found in ref. [9]. The thermal stability of expanite is generally observed to be higher for carbon than for nitrogen; this is also reflected in a higher allowable processing temperature applied in carburising as compared to nitriding.

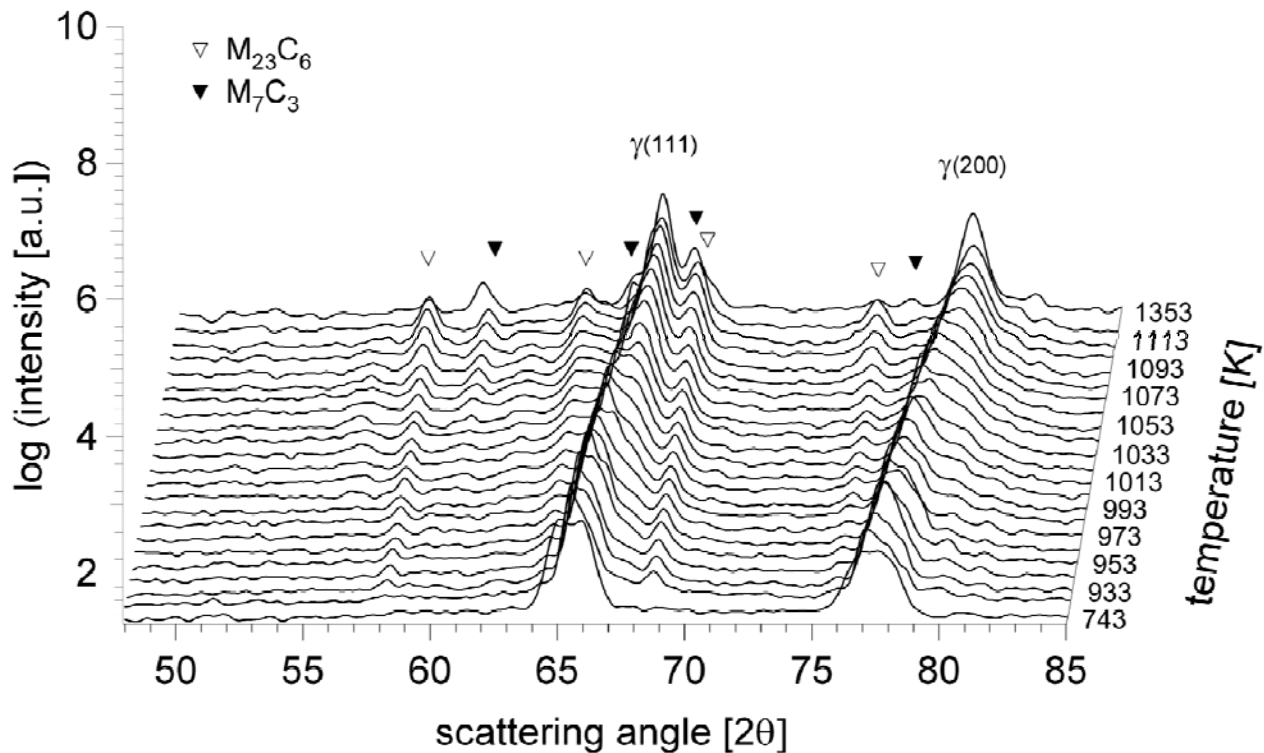


Fig. 6. X-ray diffraction patterns of carbon expanite obtained in 45μm AISI 316 powder isochronally heated to different temperatures. The powder was carburised to an overall carbon content of 2.1 wt.% (at 470°C). M in $M_{23}C_6$ and M_7C_3 represents Cr, Fe and Mo.

7. Conclusions

It is proposed that the classification “expanded austenite” or “S-phase” is replaced by expanite. Controlled dissolution of high amounts of nitrogen and carbon in stainless steel is possible; the solubility range for nitrogen in nitrogen expanite spans from $y_N = 0.17$ to 0.61 and the maximum lattice expansion can reach nearly 40 % (by volume) for nitrogen. The diffusion coefficient of nitrogen in expanite is strongly composition dependent with a maximum value in an intermediate composition range. Expanite is a metastable phase and tends to decompose into CrN (nitriding) or $M_7C_3/M_{23}C_6$ (carburising) upon prolonged thermal exposure. Examples of low temperature surface hardening of stainless steel are given.

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